

# Liquid Crystalline Copolyester/Polyethylene *In Situ* Composite Film: Rheology, Morphology, Molecular Orientation, and Tensile Properties

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Received 27 March 2001; accepted 28 July 2001

**ABSTRACT:** A thermotropic liquid crystalline copolyester (TLCP) was blended with low density polyethylene using a corotating twin screw extruder and then fabricated by extrusion through a miniextruder as cast film. Rheological behavior, morphology, and tensile properties of the blends were investigated. Melt viscosities of neat components and blends measured by using plate-and-plate and capillary rheometers at 240°C, in the shear rate range  $1\text{--}10^4\text{ s}^{-1}$ , showed similar shear thinning effect. The viscosity values measured by the two techniques in the overlapping range of shear rate are found to be identical, which is in accord with the Cox–Merz rule. Addition of TLCP slightly reduces the matrix melt viscosity. TLCP dispersed phase in the extruded strand appeared in the form of spherical droplets. These droplets were elongated into fibrils with high aspect ratio (length to width) at the film extrusion step. As a result, the Young's modulus in machine direction (MD) of the composite film was greatly enhanced. At 20 wt % of TLCP, the MD Young's modulus was found to be about 16-fold increase compared to that of the neat polyethylene film. However, the elongation at break sharply dropped with the increase of TLCP content. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 84: 561–567, 2002; DOI 10.1002/app.10307

**Key words:** liquid crystalline polymer; polyethylene; *in situ* composite; rheology; morphology; molecular orientation

## INTRODUCTION

In recent years, there has been a growing interest in the research of immiscible blends between a conventional thermoplastic and a thermotropic liquid crystalline polymer (TLCP). In the molten state, the dispersed TLCP droplets can be deformed into elongated fibrils under shear or extensional flow field. Following melt solidification,

the TLCP fibrils are frozen in the matrix and reinforce it in a similar fashion as a conventional short-fiber reinforced plastic. Thus, such a system is called an “*in situ* composite.”<sup>1</sup> The ultimate mechanical properties of the *in situ* composite are controlled by morphology, which in turn depends on the rheological behavior of the blend components, composition, interfacial tension, and processing conditions.<sup>2–4</sup> Different methods used for specimen preparation, i.e., different thermal and stress history, normally give rise to different degrees of molecular orientation in TLCP phase, thus resulting in different mechanical properties. It has been observed that TLCP fabricated in the forms of fiber, sheet, film, and molding specimens show the decline in strength due to the decrease

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Contract grant sponsor: Thailand Research Fund; contract grant number: RTA3880009.

*Journal of Applied Polymer Science*, Vol. 84, 561–567 (2002)  
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of molecular orientation.<sup>5</sup> In general, the skin-core morphology occurs in injection molding and extruded specimens.<sup>4,6</sup> Anisotropy in properties of these specimens is also observed, especially in thin films and extruded sheets, i.e. different properties are obtained when tested in the machine (MD) and in transverse directions (TD). This is due to the uniaxial orientation of the reinforcing fibers. This problem has been solved—for example, in the case of linear low density polyethylene (LLDPE)/high density polyethylene (HDPE)/TLCP film by using counterrotation die to create a crosswise structure of TLCP fibrils.<sup>7</sup>

Polyolefins are attractive plastics for use as matrices in *in situ* composites due to their several interesting properties, such as low price, good chemical resistance, good processability, toughness, flexibility, and recyclability. Various grades of polypropylene used as the matrices for different TLCP disperse phases have been reported, emphasizing the effects of processing conditions, viscosity ratio (disperse phase to matrix phase), and compatibilizers on rheology, morphology, and ultimate properties of the composites.<sup>8–15</sup> Blends of polyethylene (PE) with TLCP, on the other hand, have been reported only by a few groups.<sup>16–19</sup> This may be due to the difficulty in processing, particularly for HDPE film, due to uneven shrinkage upon solidification. In some cases, no improvement of the tensile properties of the TLCP/HDPE blend over that of the matrix was observed.<sup>18</sup> Therefore, most of the works on TLCP/HDPE *in situ* composites were emphasized on the effect of different compatibilizers.

In this work we have investigated the blend of a semiflexible TLCP with low density polyethylene (LDPE). The specimens were prepared as extruded film. *In situ* composite prepared in the form of thin film is a good model for investigation of the effect of reinforcement by uni-axially oriented TLCP fibrils. This is because no skin-core and weld-line effects occurred in the extruded film, and the mechanical properties in both machine and transverse directions can be determined separately. The effects of processing conditions and composition on rheology, morphology, molecular alignment, and tensile properties of TLCP/PE *in situ* composite are reported.

## EXPERIMENTAL

### Materials

LDPE (LD1905F) was supplied by Thai Polyethylene Co., Ltd.. The melting temperature is

115°C, and melt flow index is 5.0 g/10 min (ASTM D1238). The material has a density of 0.919 g/cm<sup>3</sup>. The TLCP, used as a dispersed phase, was a copolyester of 60 mol % *p*-hydroxy benzoic acid and 40 mol % ethylene terephthalate, trade name Rodrun LC3000, supplied by Unitika Co., Ltd. The melting temperature ( $T_m$ ) of TLCP is 220°C and the density is 1.4 g/cm<sup>3</sup>. All materials used in this study were dried in a vacuum oven at 70°C for 12 h before use.

### Blend Preparation and Film Extrusion

The film specimens were prepared in two steps. First, TLCP of varying amount was blended with PE in a corotating intermeshing twin screw extruder (PRISM TSE-16TC). Processing conditions used were the same as described elsewhere for TLCP/polypropylene (PP) blend.<sup>13,14</sup> The blends were extruded with the screw speed of 100 rpm. The extruded strand was immediately quenched in a water bath, subsequently chopped into pellets, and dried at 70°C for 12 h in a vacuum oven. In the second step, pellets of TLCP/PE blends were extruded as cast film using a 16-mm miniextruder (Randcastle RCP-0625) equipped with a cast film line. Temperatures at the hopper zone, two barrel zones and slit die were 190/215/225/240°C, respectively. The gap of the die lip and the width were fixed at 0.65 and 152 mm, respectively. The screw speed of the microtruder was set at 40 rpm. After exiting the die outlet, the film was uniaxially drawn at a various draw ratio. The highest draw ratio attained was 30 (film thickness 20  $\mu\text{m}$ ). Draw ratio (DR) is defined as  $D_0/D$ , where  $D_0$  is the die separation, and  $D$  is the thickness of the extruded film.

### Measurements

Melt viscosities of the pure components and blends were measured in the low frequency region, i.e., from 1 to 200 rad s<sup>-1</sup>, by using parallel plates rheometer (Haake Rotovisco RT 20). About 1-mm thick sheet of specimen was prepared using a hot press and cut to obtain a disk of 20-mm diameter. The viscosity measurement was carried out by using oscillatory shear mode at 240°C, which was equal to the die temperature of the film extruder. In the high shear rate region (60–10,000 s<sup>-1</sup>), the melt viscosities of all specimens were measured using a Rosand RH710 capillary rheometer at 240°C. A capillary of diameter 1 mm and length of 16 mm (L/D = 16) was used for the

viscosity measurement. The end effects (Bagley corrections) and the Rabinowitsch corrections were performed in all cases using two dies (a zero die and a 16-mm die) with flat ends, as specified for the Rosand system.

Microstructures of the blend extrudates and films were obtained by means of a scanning electron microscope (Hitachi 2500) operated with an accelerating voltage of 15 kV. Prior to examination, the specimens were dipped in liquid nitrogen for 30 min and fractured. The fractured surfaces were sputter coated with palladium for enhanced surface conductivity. Polarized optical microscope (Olympus) was also used to observe film morphology. The actual size of TLCP fibrils can also be seen when PE was dissolved away with hot xylene.

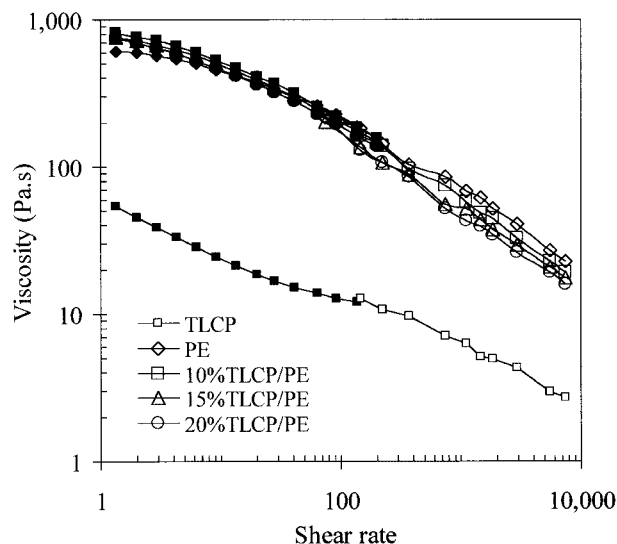
Molecular orientation of TLCP phase in the film specimen was assessed by using infrared dichroism technique.<sup>20–22</sup> The FTIR spectrometer (Perkin Elmer system 2000) equipped with an aluminum wire grid polarizer was used to record the absorption spectra with polarized direction parallel and perpendicular to the orientation (machine) direction. Each spectrum was an averaged of 16 scans at the resolution of 4 cm<sup>-1</sup>.

Tensile tests were performed on an Instron 4301. The films cut into dumbbell shape of 4-mm wide and 75-mm long (ASTM D214) were tested in both machine (MD) and transverse (TD) directions. A cross-head speed of 50 mm/min was used with a load cell of 10 N. For each sample, the mean value of at least 10 measurements was determined. Ultimate tensile strength, percent elongation at break, and Young's modulus evaluated by secant method are presented.

## RESULTS AND DISCUSSION

### Rheological Behavior

The viscosities at 240°C of the pure components and blends as a function of shear rate are presented in Figure 1. Two sets of measurements are included in the same figure, namely, the complex viscosities obtained from plate-and-plate rheometer in the low frequency region (1–200 rad s<sup>-1</sup>) and the shear viscosities measured by using the capillary rheometer in the high shear rate region (60–10,000 s<sup>-1</sup>). It is seen that all materials exhibit non-Newtonian flow behavior with strong shear thinning effect in the whole range of shear rate being investigated. That means the viscosi-



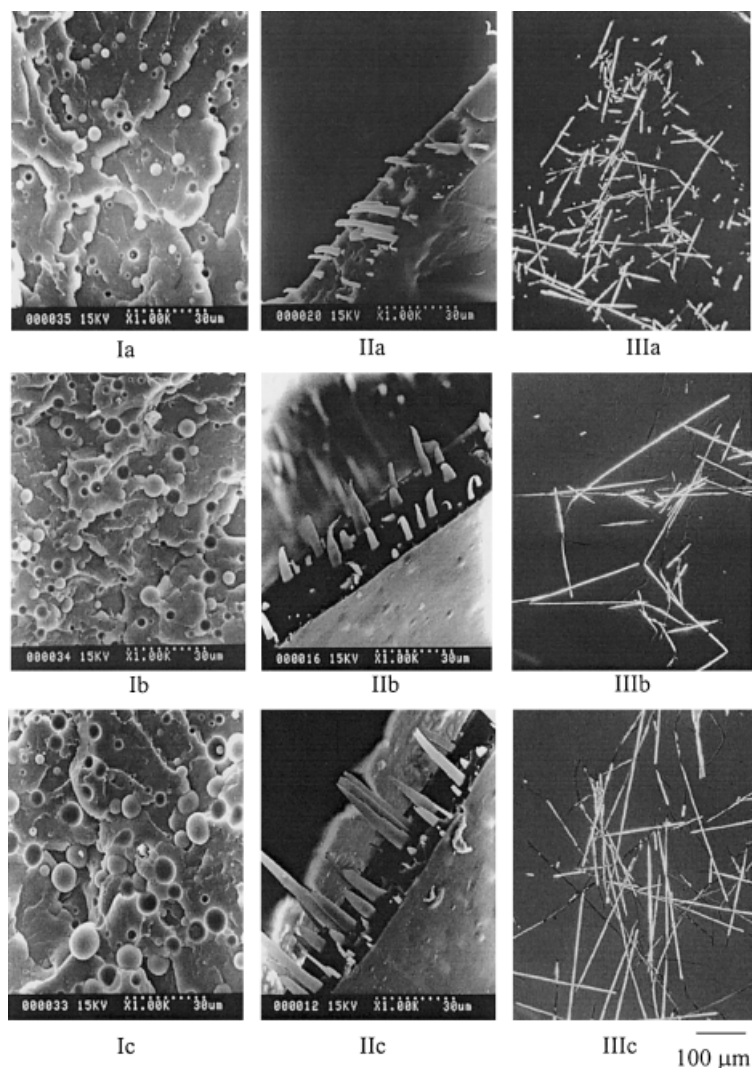
**Figure 1** Viscosities of neat PE, TLCP, and TLCP/PE blends containing 10, 1, and 20 wt % TLCP vs shear rate measured at 240°C. Filled symbols for the complex viscosity vs frequency (rad s<sup>-1</sup>) and open symbols for the shear viscosity vs shear rate (s<sup>-1</sup>).

ties of all specimens decrease with the increase of frequency or shear rate, due to the shear-induced chain orientation and thus reduction of chain entanglement.<sup>23</sup> From capillary data, the values of the exponent ( $n$ ) are calculated from the power law equation,

$$\eta = k \dot{\gamma}^{(n-1)} \quad (1)$$

where  $\eta$  = viscosity,  $\dot{\gamma}$  = shear rate, and  $k$  = viscosity when  $n = 1$ . The values of the exponents were found to be 0.6 for TLCP and 0.5 for PE and all blends. At all shear rates, the viscosity of TLCP is about two decades lower than that of the neat PE, due to the high molecular orientation and less entanglement in the nematic phase. Incorporation of TLCP slightly reduces the viscosity of the matrix in the high shear rate region. This is derived from the low viscosity of TLCP and the high deformability of TLCP domains at high shear rate. With increasing amount of TLCP, the viscosity of the blend slightly decreases further. When closely looked at the middle of the flow curves, i.e., in the overlapping shear rate region measured by using the two techniques, the values of complex viscosity ( $\eta^*$ ) and shear viscosity ( $\eta$ ) are about the same. These results are in accord with the Cox–Merz rule,<sup>24</sup>

$$|\eta^*(\omega)| = \eta(\dot{\gamma}) \quad (\omega = \dot{\gamma}) \quad (2)$$



**Figure 2** SEM micrographs of fracture surfaces of extruded strands (Column I), extruded films (Column II), and optical micrographs of extracted TLCP fibrils (Column III): from TLCP/PE blends with TLCP content of (a) 10, (b) 15, and (c) 20 wt %.

The rule states that the curve of complex viscosity as a function of frequency ( $\omega$ ) is identical to the curve of shear viscosity as a function of shear rate ( $\dot{\gamma}$ ). This rule has been found to be reliable for flexible polymers, but fails for some rigid polymers and some polyethylene systems.<sup>25,26</sup>

The viscosity ratio, defined as the ratio of the viscosity of TLCP to that of PE,  $\eta_{\text{TLCP}}/\eta_{\text{PE}}$ , lied in the range of 0.04–0.15 over the whole region of shear rate being measured. These values are approximately in the same range as those obtained for TLCP/PP systems reported earlier by our group.<sup>14</sup>

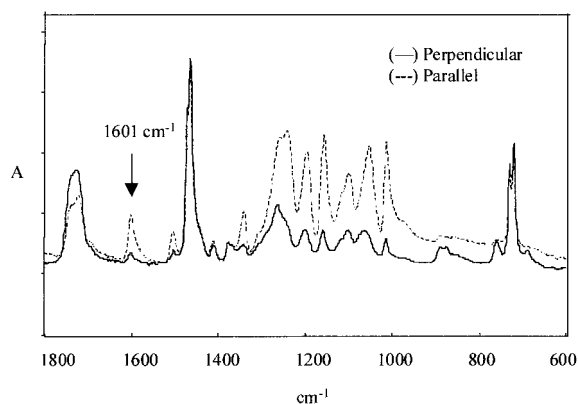
### Morphology

The morphology of different specimens shown in Figure 2 is presented in three columns for com-

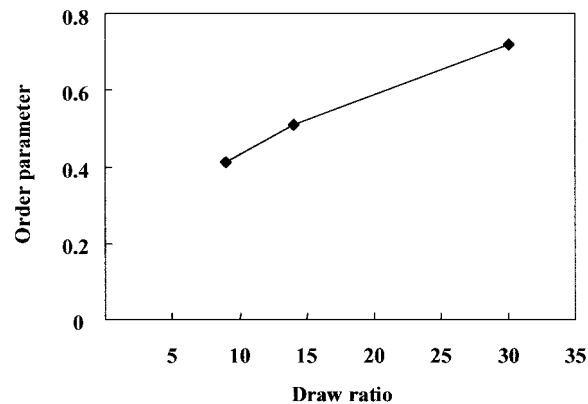
parison. Each column shows the results obtained from the blends containing (a) 10 wt %, (b) 15 wt %, and (c) 20 wt % TLCP. Column I illustrates the scanning electron microscopy (SEM) micrographs ( $\times 1000$  magnification) of fracture surfaces of the strands extruded from the twin screw extruder. Column II presents the fracture surfaces of the extruded films at the draw ratio of 30. Optical micrographs shown in column III are TLCP fibrils extracted from the corresponding films derived from column II. TLCP domains in the extruded strands (Column I) appear in the form of spherical droplets of various sizes. The average diameter of TLCP droplet grows with increasing TLCP content. The diameters of the large TLCP droplets could be estimated to be about 5, 7, and 11  $\mu\text{m}$



for the blends containing 10, 15, and 20 wt % TLCP, respectively. This is attributed to the higher possibility for the droplets to coalesce as the TLCP content increases, resulting in coarsening blend morphology. Fracture surfaces of the films presented in Column II reveal that the TLCP droplets are now greatly deformed into fibrils at the step of film extrusion, which it has been drawn at the draw ratio of 30. Fiber pull-out feature of the film fracture surfaces is evidence of poor interfacial adhesion between the two phases. Long pull-out fibers with the width up to about 6  $\mu\text{m}$  are seen in 20 wt % TLCP/PE film fracture. These fibrils are somewhat flattened due to the extrusion through a narrow slit die. Therefore, the width of these fibers as seen from the side view seems to be approximately the same as the diameter of droplets in the extruded strands. Furthermore, coalescence of some elongated droplets might occur during extrusion of cast film. To investigate the actual fiber length and aspect ratio, the PE matrix was dissolved away using hot xylene. The remaining TLCP fibrils were observed under a polarized optical microscope as shown in Column III ( $\times 100$  magnification). It can be seen that longer fibrils are generated in the blend with higher TLCP content. At 10 wt % TLCP, the length of fibrils formed varies greatly, whereas long fibrils with an aspect ratio in the range of 50–70 are formed in the blend containing 20 wt % TLCP. The reinforcing fibers with higher aspect ratio will provide more effective transfer of stress at the interface, so they are expected to improve the mechanical properties of the composites.



**Figure 3** Polarized FTIR spectra of the 10 wt % TLCP/PE *in situ* composite film: (—) perpendicular polarization; (---) parallel polarization.



**Figure 4** Effect of film draw ratio on the order parameter,  $S$ , of TLCP phase in 10 wt % TLCP/PE film.

### Molecular Orientation

Infrared dichroism technique is one of the most convenient methods that can be used to quantify the degree of molecular orientation in the film specimen. The order parameter ( $S$ ) was calculated from the dichroic ratio ( $R$ ) of the peak at  $1601\text{ cm}^{-1}$ , which is a parallel band assigned to the stretching mode of  $-\text{C}=\text{C}-$  in the benzene ring. For a band whose transition moment is parallel to the major axis of the molecule (parallel band),

$$S = \frac{(R - 1)}{(R + 1)} \quad (3)$$

where  $R = A_{\parallel}/A_{\perp}$ ;  $A_{\parallel}$  and  $A_{\perp}$  are absorbances for plane polarized light with the electric vector parallel and perpendicular to the preferred direction (machine direction), respectively. The typical polarized FTIR spectra of 10 wt % TLCP/PE film are illustrated in Figure 3. Two spectra shown in this figure were recorded with the polarizer aligned parallel (broken line) and perpendicular (full line) to the direction of orientation (machine direction) of the film drawn at the draw ratio of 30.

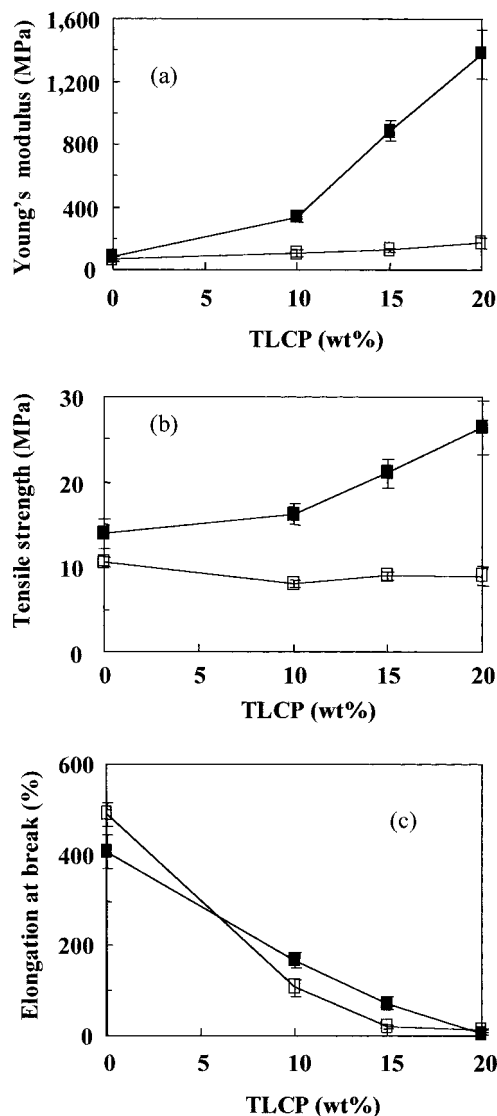
Figure 4 is the plot of the order parameter of TLCP phase in 10 wt % TLCP/PE film vs the draw ratio. It is clearly seen that the order parameter almost linearly increases from about 0.4 to 0.7 as the film draw ratio increases from 9 to 30. The higher the draw ratio, the greater the extensional load, forcing the molecules to align more effectively in the flow direction. The order parameters of the TLCP phase in the films containing 15 and 20 wt % TLCP at the draw ratio of 30 were also determined and found to be approximately the

same, i.e., 0.7. Though the aspect ratio of the TLCP fibrils grows with the increase TLCP content as seen in Figure 2, Column III, the molecular orientation in TLCP fibrils remains the same. This implies that the molecular orientation in TLCP phase depends only on the extensional load but not on the amount of TLCP. On the other hand, the TLCP fiber aspect ratio depends on both extensional load and TLCP content. Variation of the screw speeds in the first mixing step, which resulted in different degrees of dispersion, had no influence on the order parameter because the elongation of TLCP domains took place in the second step when the film was drawn.

### Tensile Properties

The optimum conditions for preparation of TLCP/PE blend was by operating at a screw speed of 100 rpm in the twin screw extruder and the film was extruded in the miniextruder at the screw speed of 40 rpm. Figure 5 shows tensile properties of the neat PE and composite films drawn at the draw ratio of 30. The Young's modulus, ultimate tensile strength, and percent elongation at break tested in both TD and MD directions are plotted as a function of TLCP content [see Fig. 5(a), (b), and (c), respectively]. The MD Young's modulus of TLCP/PE composite film shows dramatic improvement with addition of TLCP. The values of MD Young's moduli of the neat PE and composites containing 10, 15, and 20 wt % TLCP are 82, 341, 885, and 1,374 MPa, respectively. This means the MD moduli of the composites are about 4-fold, 11-fold, and 16-fold increase as compared to the neat PE. On the other hand, the TD modulus shows only a slight increase with addition of TLCP. Hence the anisotropy in the values of moduli is greatly enhanced at 20% TLCP content. Figure 5(b) also shows that the tensile strength of composite films tested in machine direction is higher than that in the transverse direction. With addition of TLCP, the MD tensile strength increases, but the TD value slightly reduces. At 20 wt % TLCP content, the MD tensile strength is about twice that of the matrix. Elongation at break in both MD and TD directions are sharply dropped, as seen in Figure 5c. Especially at 20 wt % TLCP content, the elongation at break is only about 5%.

The addition of TLCP into PE matrix results in an increase of the MD modulus and tensile strength of TLCP/PE composite films. This is due to the reinforcement of the uniaxially oriented



**Figure 5** Effect of TLCP content on tensile properties of TLCP/PE *in situ* composite films: (a) Young's modulus, (b) tensile strength, and (c) elongation at break, (■) in machine direction and (□) in transverse direction

high-strength TLCP fibrils. From the morphology of the specimens shown in Figure 2, it is clear that higher TLCP content gives rise to higher number of reinforcing fibers with higher aspect ratio. These two factors provided more efficient transfer of stress at the interface, and therefore the modulus in MD greatly increased. Most of the published papers have shown improved reinforcement with addition of TLCP to an isotropic polymer. Although the magnitude of the reinforcement and the dependence on TLCP content varied, the general trends of tensile properties were observed: dramatic increases in the tensile

modulus, with smaller increase in tensile strength, accompanied by a substantial decrease in elongation at break.

## CONCLUSION

Shear thinning behavior was observed in all neat components and blends. Within the shear rate range  $1\text{--}10^4\text{ s}^{-1}$ , the viscosity ratio of TLCP to PE was found to be very low, i.e., in the range 0.04—0.15. In the first mixing step, the TLCP dispersed phase as observed in the extruded strand was in the form of spherical droplets of various sizes, which grew with the increase of TLCP content. However, after the blend was extruded as cast film with high draw ratio, TLCP could be deformed into long fibrils with increasing aspect ratio as TLCP content increased. And the molecular orientation in TLCP phase was found to improve with the increase of film draw ratio. These results led to a dramatic increase of the film MD Young's modulus. For 20 wt % TLCP/PE film, the MD modulus increased up to 16-fold of the value of neat PE film. The MD tensile strength increased twice that of the neat PE, but the elongation at break in both directions dropped sharply.

This research was financially supported by the Thailand Research Fund (RTA3880009). We are indebted to the Alexander von Humboldt Foundation for the donation of plate-plate rheometer. And we also would like to thank the Faculty of Science and Technology, Prince of Songkla University, Pattani, for permission to use capillary rheometer.

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